Design of Recycling System for Spent Rinse Water from Sandia's Microelectronics Development Laboratory (MDL)

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Abstract

The steps taken at Sandia to install a system for recycling spent rinse waters from its semiconductor fab consisted of the following sequence: 1.) Classifying the properties of the water discharged from all fab wet stations; 2.) Installing a drain system and tank to collect discharge waters from those stations deemed most compatible with recycling; 3.) Instrumenting the tank and its feed lines for monitoring the properties of the collected water; 4.) Writing software for data logging and controlling the system operation; and 5.) Collecting data to characterize the water quality and to identify the most favorable node for returning the collected water to the UPW system. Yet to be completed is the final loop that returns the water to the UPW system and completes the recycle installation.

Introduction

Recycling of spent rinse waters from wet processes -- the reintroduction of these spent rinse waters as feedwater to some node of the plant ultrapure water (UPW) system -- is an effective but at present underutilized tactic for reducing the demand made by semiconductor manufacturing upon regional water supplies. While the high quality of the rinse waters being discharged from wet benches is widely acknowledged, so also is the risk perceived to be associated with the adoption of recycling these spent rinse waters which, in spite of their overall high quality, often contain trace species not found in the feed water supplied to the plant by a municipal utility. Several past recycling experiences, for the most part not formally reported or documented, include stories in which contaminants in the recycled rinse water were suspected of having a deleterious impact upon the components of the UPW system or, worse yet, the product wafers themselves. Water recycling thus acquired the reputation of being a risky undertaking with potentially severe penalties and only limited secondary benefits. The safer course, still being followed by many industry leaders, remains avoiding these potential pitfalls by avoiding water recycling.

The goal of the work reported here is the design, installation and operation of a "bullet-proof" water recycle system that avoids the mistakes of the past and helps to convince the industry that the problems previously encountered in water recycling are no longer a threat to production and no longer a valid basis for rejecting water recycling in the new millennium. Indeed the 1997 edition of the National Technology Roadmap for Semiconductors (NTRS) specifies target values of net water usage and UPW water usage, both measured per unit area of silicon produced, that can be achieved only by recycling [Ref. 1].

Background

The initial step of this project was to classify the 50 water discharge streams from Sandia's Microelectronics Development Laboratory (MDL) fab into one of three categories: 1.) Those streams deemed easy to recycle (Class "C" [for Collectible]); 2.) Those streams perceived to be difficult to recycle (Class "R" [for Reject]); and 3.) Those streams not able to be confidently assigned to either of the first two categories because of insufficient information regarding their compositions and concentrations (Class "Q" [for Questionable]). The criteria for classifying a stream as Class C (Table 1) were:

1.) Spent rinse water from wet cleaning steps consisting of only inorganic reagents; or

2.) Spent rinse water from a Spin/Rinse/Dry station that follows a process step thought to be free of slurry residues or other solids.

These water discharge streams were expected to contain only constituents that are easily removed by the purification modules of the UPW plant. They seem suitable for collecting into a common recycle tank without the need for any preconditioning or separate purification.

Table 1 lists 20 individual streams from the MDL classified as "C" streams. Only those 13 of the 20 C stations marked with an asterisk were part of the initial collection system installed in the MDL. These 13 C* streams are centrally located in the MDL fab and discharge as much as 40% of the fab water now sent to the Acid Waste Neutralization (AWN) tank. The seven C streams not included in the initial collection system for recycle are more remote to the central location of the collection tank and account for only a minor fraction of the MDL water discharge.

The R classification (Table 2) was assigned to:

1.) Any discharge stream containing organic chemicals, including the water from a rinse that follows an organic solvent cleaning step;

2.) Those streams having high solids content such as post CMP rinses; and

3.) Those streams expected to have high concentrations of metals.

Streams with an "R" classification present the most difficult challenges for recycling with the highest risk for introducing an upset into the UPW plant. They are not part of the MDL recycle plans at present.

The remaining "Q" streams (Table 3) from the fab will eventually be characterized individually, using: 1.) On-line instrumentation similar to that monitoring the input to the "C*" stream collection tank; 2.) Off-line instrumentation similar to that used in the grab sample analyses described in a following section of this report (Tables 4 - 9); and 3.) Any on-line, speciating, organic sensor prototype that might become available. None of these "Q" streams are being collected at present. The type and concentration of contamination in each stream will define the properties of the purification modules needed, if any, before adding that "Q" stream to the collection tank of the recycling loop.

Description of the Initial, Single-Tank Recycle System Installation

PVC drain pipes were connected to the existing drains from the wet benches through a manually operated three-way valve which can direct the water discharge from each wet bench plenum to either the existing AWN tank or to the 1000 gallon collection tank newly installed as part of the initial recycle loop. Rinse water flow to the collection tank, located in the sub fab area, is by gravity. The collection tank is double walled, the inner wall being made of polypropylene and the outer, secondary containment, of fiberglass. Penetrations through the top of the tank allowed the insertion of resistivity, pH and oxidation-reduction potential (ORP) cells directly into the collected water. An ultrasonic sensor extending through the top of the tank continuously measures the water level.

Figure 1 is a schematic of the single tank recycle system presently installed in the basement of the MDL. Spent rinse water enters the collection tank through the incoming line in the direction of the arrow ("Feedline from Fab", upper right hand corner of the diagram). In the automatic mode of the recycle system, when the water level in the collection tank reaches 100%, the recycle pump turns on, transporting water from the bottom of the tank (lower left hand side of the tank, Fig. 1) through the exit lines and flowmeter. This line leads to a downstream three-way valve (not shown) which directs the water to either a recycle node of the UPW system or diverts it from the recycle node to the AWN. The recycle pump turns off when the water level in the collection tank falls to about 83%, having emptied approximately 170 gallons from the tank. This emptying/filling action cycles continuously in the automatic operating mode so that the water volume in the collection tank oscillates between 830 and 1000 gallons. The recycle pump-on and pump-off times, in conjunction with the measured flow rate in the recycle line, are used to calculate an average rinse water flowrate from the fab to the collection tank. This value in turn is used to sum the total volume of water exiting the collection tank through the recycle line over a given time period.

An icon depicting a two-position switch and a pump on/off indicator light (left hand side of Fig. 1, below the flowmeter box) show whether the recycle pump is on or off. If the pump switch light, below the pump on/off indicator light, is off, the automatic cycling of the recycle pump just described is disarmed and the pump operation is controlled manually.

The tank has an overflow line, shown at the upper left-hand side of the tank (Fig. 1), which prevents water accumulation in the collection tank from exceeding 100%. Water above this level drains by gravity to the AWN tank. On the right hand side of the collection tank is a recirculation pump and loop whose purpose is to promote mixing of the tank contents by recirculating the tank water through a closed, high flow loop.

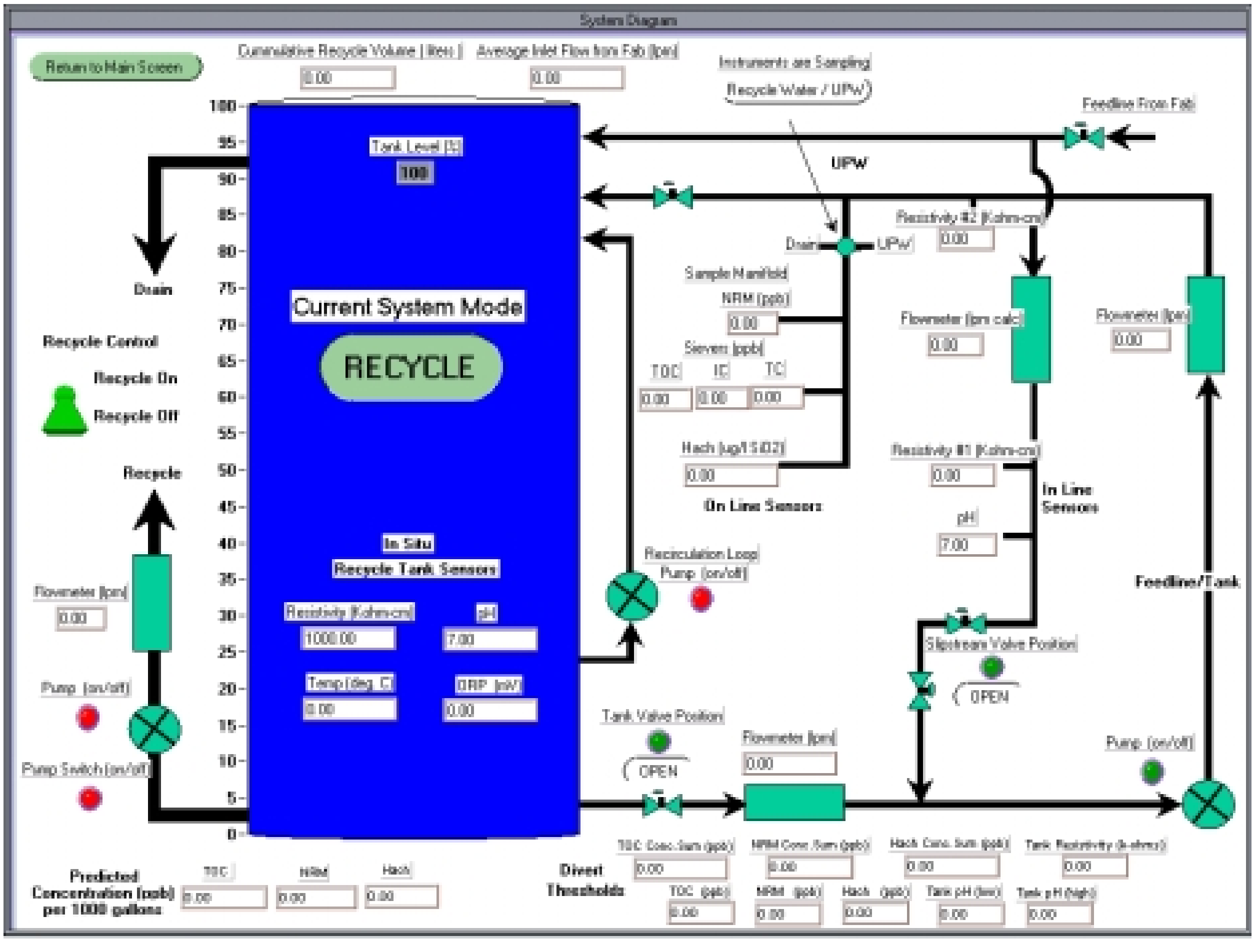

Figure 1. Collection Tank/Monitoring System Schematic

<u>Monitoring/Control Instrumentation</u>

The properties of both the incoming water and the water in the collection tank are measured and logged by both in-line and on-line analyzers in the sampling manifold and by *in situ* sensors within the collection tank. A tee junction in the incoming rinse water line (upper right hand corner, Fig. 1) feeds a sample slipstream into the sampling manifold, which includes two in-line resistivity cells (labeled #1 and #2), a pH cell, a pump and a flowmeter. Downstream of the pump and flowmeter is a second tee junction for delivering a pressurized slip stream to on-line analyzers for measuring total oxidizable carbon (TOC), nonvolatile residue (NVR) and dissolved silica. All instrumentation used is commercially available:

In-line Analyzers

Resistivity cells (Thornton Model 354-203 with 770 readout)

pH cell (Thornton 353-421 Smart pH Sensor)

Flow meters (Signet Models P51530)

On-line Analyzers for

TOC (Sievers' 800 Turbo with an upstream inorganic removal module)

NVR (PMS 7700 Liquitrak)

Dissolved silica (Hach Series 5000)

In situ (in collection tank)

Resistivity cell (Thornton 354-203 with 770 readout)

pH cell (Thornton 353-421 Smart pH Sensor)

Oxidation-reduction potential (ORP) cell (Thornton 353-521)

Temperature (Thornton 354-203)

Liquid level sensor (Flowline Controller and Transmitter, Models LC52 and LU30, respectively)

As sketched in Figure 1, the system plumbing and valving enables the water stream sampled by the in-line and on-line analyzers in the sampling manifold to be one of the following: 1.) Incoming rinse water only; 2.) Collection tank water only; or 3.) A combination of the two. The *in situ* analyzers measure the properties of just the water accumulating in the collection tank.

All these analyzers measure and report data continuously. The responses of the resistivity, pH, temperature and ORP cells are assumed to be instantaneous and to represent real-time measurements. The same is true for the ultrasonic liquid level sensor. Any time delays between measurement and readout of these analyzers are ignored.

The on-line analyzers, on the other hand, all have non-negligible response times (time to reach 90% of the steady state value following a step change in the value of the input parameter being measured). Nominal values of the response times of the on-line analyzers are:

TOC: 200 s

NVR: 300 s

Dissolved silica: 480 s

Control strategy in a single tank recycle system must take account of these delays in the detection of contaminants by the on-line analyzers.

Operating Modes/Recycle System Control Strategy

The role of the analyzers in the recycle system is to determine the suitability of the collected rinse waters for recycling and to generate control signals that direct the water exiting the collection tank to either a UPW system node or to the AWN. The recycle/divert decisions depend upon comparing current values of the following data with predetermined threshold values: 1.) real time values of the resistivity and pH cells in the tank; 2.) expected tank values of TOC, NVR and dissolved silica predicted by a weighting/summing procedure of the concentrations measured over each 1000 gallon increment of entering feed water; and 3.) maximum acceptable, one-time concentrations of TOC, NVR or dissolved silica. Nine values of divert thresholds appear in the bottom right side of Figure 1: minimum tank resistivity; high and low limitations for tank pH; a maximum allowable, one-time value of concentration for each of the three on-line analyzers (TOC, NVR and dissolved silica); and a maximum value of expected concentration for each of the three on-line analyzers as predicted by a summing procedure described below. The system diagram also displays the current values of predicted tank TOC, NVR and dissolved silica (bottom left, Fig. 1). The program as written contains default values but each of the nine divert thresholds can be changed by the operator during the startup procedure.

In the single collection tank design installed in the MDL, the on-line analyzers sample only the incoming water when the operating mode of the recycle system is recycling water to the UPW system (the recycle mode). When the recycle system is in the divert mode, the on-line analyzers sample only tank water. When starting with an empty collection tank, or when restarting the control software program, the recycle system is in the divert mode. The initial readings of the *in situ* tank sensors and the on-line analyzers in the sampling manifold are then compared with the nine predetermined divert threshold values. The recycle system will not switch to the recycle mode unless all analyzers are within their assigned threshold ranges for 10 minutes. Any analyzer reading that is not within its predetermined, acceptable range initiates a new 10-minute test period.

When the collection tank is empty, the typical inlet flow rate of 40 gpm takes about 25 minutes to fill the collection tank. By the time it is full, the recycle system will have switched to its recycle mode, assuming all analyzers are in the green. Until the tank reaches its 100% level, the recycle pump remains off even in the recycle mode and no water leaves the tank.

In the recycle mode, the **on-line** analyzers measure contaminant concentrations in only the incoming rinse water. These concentrations are logged as averages over 30 s intervals. The 30 s averages are weighted by the volume of water flowing into the collection tank over the same 30 s time interval, yielding the contaminant mass introduced into the collection tank during that 30 s interval. These values of contaminant mass are summed over the number of 30 s intervals needed to feed 1000 gallons of rinse water into the collection tank. This mass value is converted into a concentration that is displayed as a predicted contaminant concentration (lower left, Fig. 1). When the predicted concentration of any one of the three on-line analyzers, as calculated by the summing procedure, exceeds the divert threshold concentration for that analyzer, water flow from the collection tank is diverted from the UPW system to the AWN. A running total of predicted contaminant concentration in the collection tank, calculated by this summing procedure, is maintained by adding each new 30 s contribution to the calculation and dropping the oldest entry in the sum.

Divert signals based on resistivity, pH and ORP depend on the readings of just the *in situ* tank sensors with respect to the predetermined divert threshold values. Three consecutive 3 s averages outside the acceptable range trigger a control signal to switch the recycle system to the divert mode.

In addition to switching the downstream three-way valve from recycle to AWN, a divert signal turns off the recycle pump, switches the on-line instruments of the sampling manifold to sample tank water only and starts the recirculation pump. The recirculation pump remains on until the recycle system returns from the divert mode to the recycle mode. During this period the in-line analyzers in the sampling manifold are filled with stagnant water and provide no useful information.

Before returning the recycle system to the recycle mode after a divert episode, all *in situ* and on-line analyzers must report values that are within their assigned ranges for a minimum of 10 minutes, as in the startup procedure. Any reading outside any of the assigned ranges restarts the 10-minute test period. When the 10-minute requirement has been met, the in-line and on-line analyzers are switched back to monitoring just the incoming rinse water as in the original startup phase. The measured concentrations of the water at the end of the 10 min period that triggered the generation of the return-to-recycle signal serve as the starting concentrations for the new summing procedure for predicting tank contaminant concentrations from the contaminant concentrations in the entering rinse water.

The recirculation pump is also turned off when the recycle system returns to its recycle mode and the recycle pump resumes its automatic operation.

Figure 2 is a flowchart, summarizing the sequence of steps in the operation and control of the Sandia recycle system. After starting the program, the operator presses the start data acquisition button on the starting screen, initiating the collection of data from all sensors and analyzers and displaying the first analyzer check screen. Each of the three on-line analyzers has its own check screen which displays its status and confirms that data collection is underway. A continue button on each analyzer's check screen triggers sequencing from one analyzer to the next, returning after the third screen to the starting screen. The operator then presses the button for the recycle system diagram (Fig. 1) and flips the recycle control switch on that screen to ON. The divert threshold values appear with default values, which can be changed, or not. The recycle system automatically starts or restarts in the divert mode, collecting data from all sensors and analyzers. Once all analyzers have reported values within their assigned ranges for 10 minutes, the system switches to its recycle mode and remains in that mode until one (or more) of the nine divert threshold values is breached. The system then reverts to its divert mode and remains there until the 10 minute requirement has again been satisfied. The steps enclosed in the dashed box of Figure 2 require no operator prompts -- they are automatically carried out.

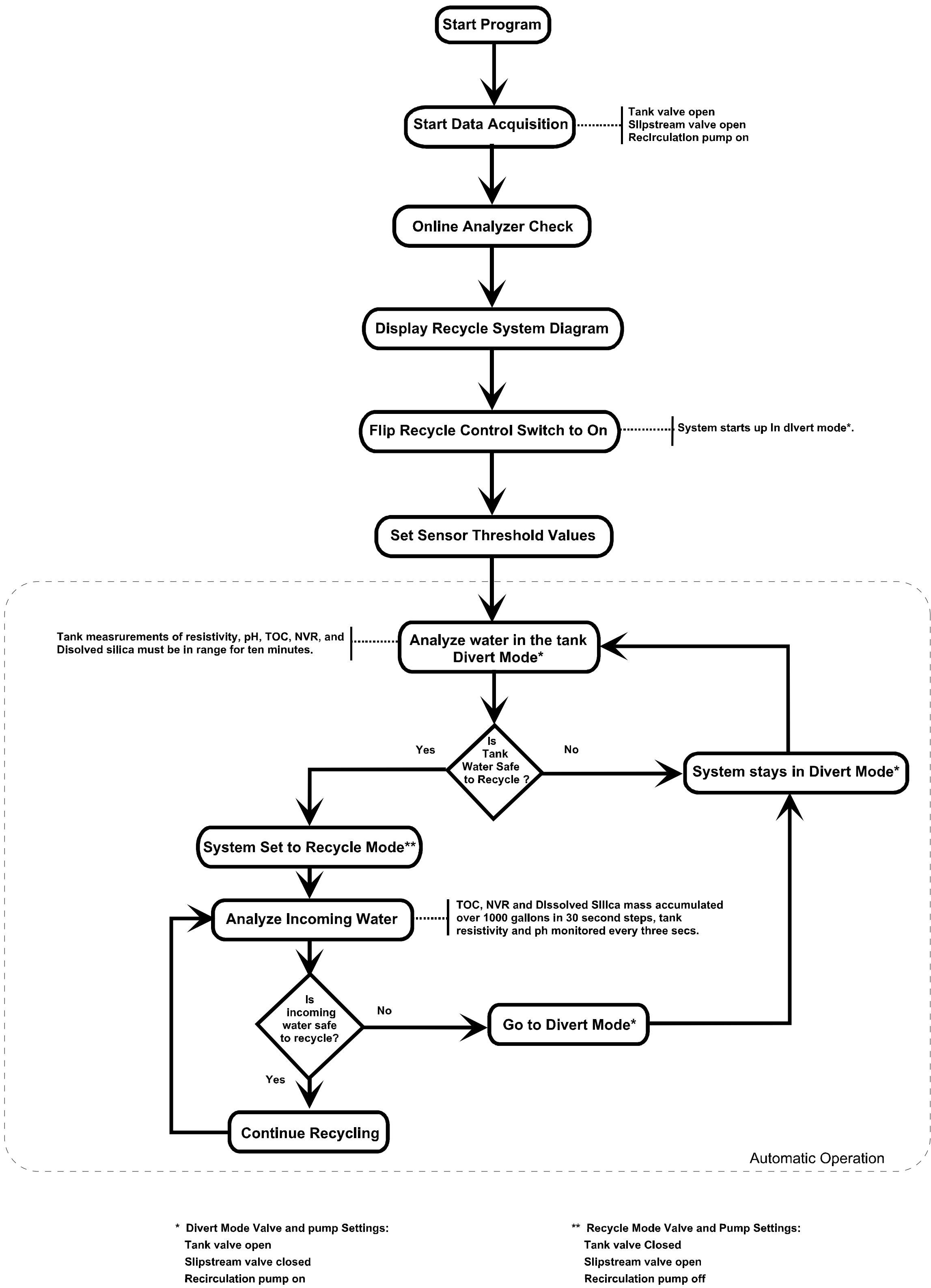

Figure 2. Recycle System Flowchart

Measured Properties of the Sandia Single Tank Recycle System

The success of a single tank recycle system depends on being able to retain control of the collected water until the analyzers complete their analyses and have time to generate a divert signal when warranted. The water being evaluated must still be available for control by the time the analyzers reach a decision. Response times of the analyzers are known. What also needs to be known is the transit time of the rinse water between its time of arrival at the on-line analyzers and its exit through the recycle pump line. This section reports measurements of such transit times.

In a set of measurements to determine the delay time between the detection of a contaminant by the in-line and on-line analyzers in the sampling manifold and its detection by the *in situ* analyzers within the collection tank, spikes of acetic acid were deliberately added to the water flowing from the closest wet bench. Acetic acid has the desirable property of being a commonly used reagent in semiconductor processing and is also a contaminant that is readily detected by resistivity, pH, ORP and TOC sensors.

The experimental procedure began during off-hours when no actual processing was underway in the fab. At these times, the water discharged to the recycle system is simply the idle UPW flow through the wet benches. Water resistivity is usually > 1 MΩ-cm, TOC is usually < 20 ppb and the pH is 5.5 -6.0. The background concentrations are thus low with respect to those encountered by the addition of even a modest contaminant spike. Typical spikes were 0.6 - 1.8 liters of concentrated glacial acetic acid, dumped rapidly into the selected wet bench plenum.

The normal configuration of the recycling system in its recycle mode is to operate with the sampling manifold sampling incoming water only and with the recirculation pump OFF. This was the configuration initially used in the delay time tests. The delay time to be measured was defined to be the time difference between the detection of the spike by in-line resistivity cell #1 and by the pH cell in the sampling manifold and the detection of the same spike by the *in situ* resistivity, ORP and pH cells within the tank.

With the recycle pump OFF and a full tank overflowing to drain, a typical delay time measured by the method just described was on the order of 70 s. The location of the *in situ* sensors is about 24 inches above the line leading to the recycle pump so that the time before the entering spike is pumped to the recycle line is somewhat longer. In addition the lines of the sampling manifold delay the arrival of the spike at resistivity cell #1 by approximately 10 s; that is, the spike enters the tank about 10 s before it reaches resistivity cell #1. The time between spike entry and its detection by the *in situ* resistivity cell is thus estimated to be about 80 s.

When the recirculation pump was ON, the delay time measured by this method was about 50% shorter -- about 35 s.

A second measurement of delay time consisted of switching the sampling manifold from incoming water only to tank water only immediately after the spike was detected by in-line resistivity cell #1. The delay time measured by this method is the difference between the detection of the incoming spike by resistivity cell #2 and the detection of the same spike by the same resistivity cell after it exits the tank via the feedline/tank line of the sampling manifold. This time delay was on the order of 300 s (recirculation pump OFF) based on the time for the full impact of the spike (resistivity cell #2 reads the same as the tank resistivity cell) to reach resistivity cell #2 via the feedline/tank route. However, the leading edge of the spike moved through the tank significantly faster, reaching resistivity cell #2 about 150 s after first being detected in the sampling line.

When the same measurement was made with the recirculation pump ON, the time required for the resistivity of cell #2 to match the tank resistivity was about 100 s, while the leading edge of the spike reached cell #2 about 70 s after the incoming spike (Figure 3).

TOC detection in the sampling manifold typically lagged the detection of the resistivity spike in the sampling manifold by about 200 s, a time in excess of the delay time measured between sampling manifold resistivity cell #1 and the tank resistivity cell. This 200 s delay in detecting a TOC spike is also longer than the delay time between a spike detected in the incoming water by resistivity cell #2 and the first indication of that spike in the outgoing tank water also as detected by resistivity cell #2. These time comparisons imply that by the time a TOC spike is detected in the sampling manifold, its leading edge will probably be exiting the collection tank through the recycle pump. While the water volume in the collection tank provides some protection by diluting high concentration spikes, this single tank recycle operation provides only marginal protection against upsets by sudden, massive organic spikes, an unacceptable shortcoming. Under the present single tank design and configuration, the only remaining protection rests in the

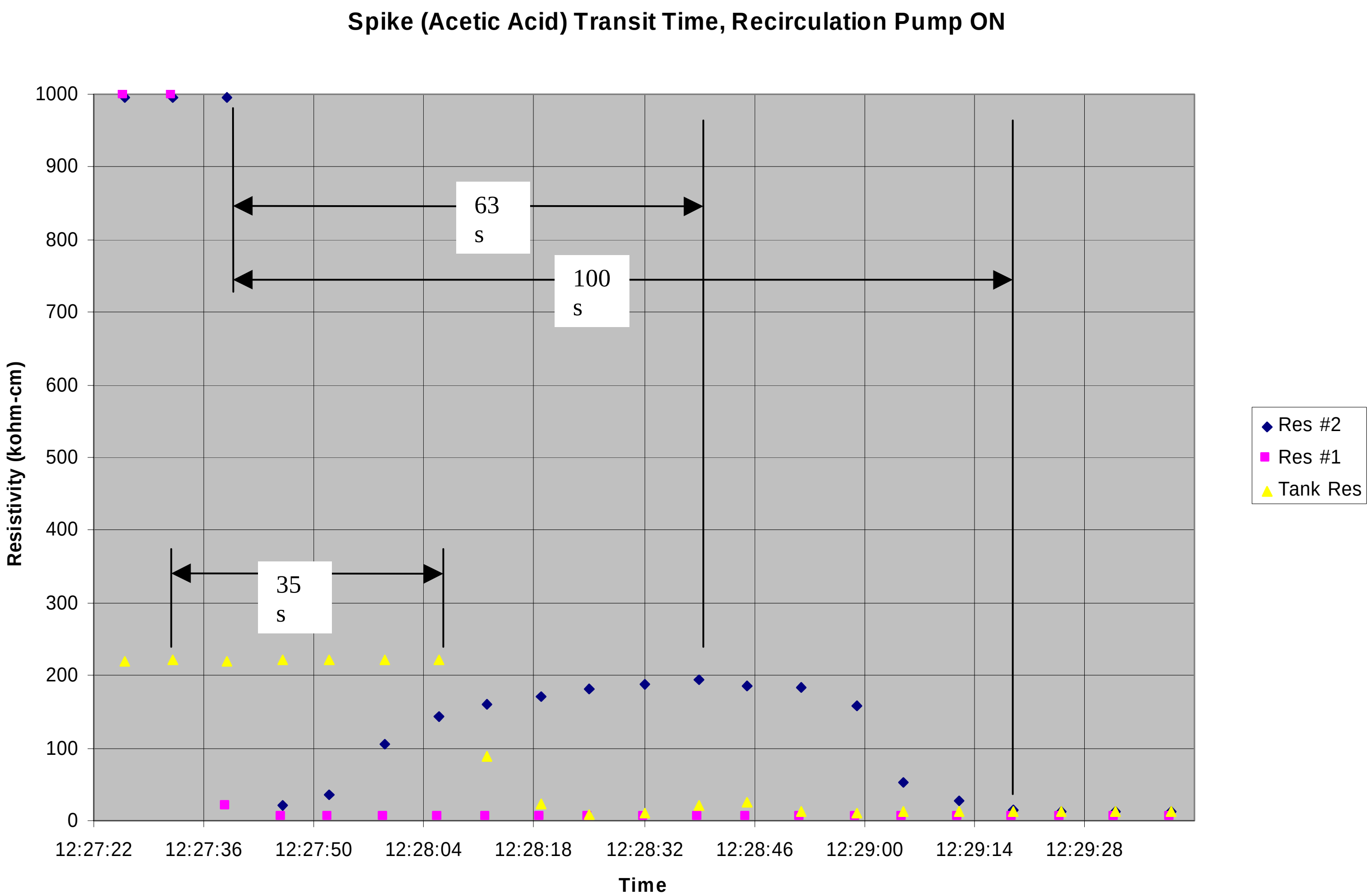

Figure 3. Measurement of Spike Transport through the Collection Tank

transit time between the collection tank and the downstream divert valve. This transit time plus the delay time between spike entry and exit from the collection tank must be greater than the response time of the TOC analyzer in order to guarantee that sudden increases in TOC concentrations above the one time, maximum threshold value will be diverted before reaching the recycle node.

To adequately protect the recycle operation, the slower responding NVR and dissolved silica analyzers require even longer transit times between the arrival of a sharp contaminant spike at the analyzer inputs and its arrival at the downstream divert valve.

Thus, while slowly rising excursions in the concentration of these contaminants can be adequately detected and diverted, the present single tank design does not provide adequate protection in the presence of contamination spikes of high concentrations and rapid rise times. The problem is that contaminant transport within the collection tank is more rapid than anticipated even under conditions that minimize convective flow. The discharge of the gravity-fed rinse water into the tank evidently either contributes enough mixing and stirring of the tank contents to rapidly eliminate contaminant concentration gradients or creates rapidly penetrating streamlines within the tank or both. Thus, in its present configuration, the Sandia single tank recycle design requires modification before bullet proof recycling can begin. No rinse water is yet being recycled.

An obvious, alternative recycling strategy is to design the recycling system to include two or three collection tanks, plumbed in parallel but filled sequentially one after the other. This arrangement greatly lengthens the storage time available for assessing the quality of the collected rinse water and determining its suitability for recycling. The longer time available for assessing the water quality lessens the dependence of the control system upon the response times of the analyzers. For example, with two collection tanks, one tank can be filling while the contents of the second tank, previously filled, are evaluated before recycling to the UPW system. With suitable volume and pumping rates, the second tank can be analyzed and emptied in time to accept the incoming rinse water once the first tank is full. The roles of the tanks are then switched. Alternatively, a three-tank arrangement allows the three actions to be carried out in parallel: one tank filling; a second full tank being analyzed; and the third tank feeding its already analyzed contents to the plant UPW system. With suitable tank sizing, analytical timing and pumping rates, these roles can rotate in series among the three tanks, providing recycled water continuously to the UPW system.

Rinse water collection with multiple tanks clearly introduces desirable, additional control into a recycle system and is a lower risk design in building a new fab. Such designs, however, may not always be compatible with the space limitations typical of retrofit installations in already built and operating facilities. At such sites, restricted to a single tank configuration, one option is to construct the collection tank with baffles and flow restrictions that lengthen the transit time between rinse water entry and exit. A single tank with multiple compartments inside could stretch the water transit time through the tank to be nearly the same as the time required to fill the empty tank. This type of construction increases tank cost but at certain sites could be the preferred solution.

Representative Properties of the Rinse Waters Being Collected

While the final configuration of Sandia's recycle system remains unsettled, considerable data have been collected and logged. This section summarizes and categorizes the properties of these monitored spent rinse waters.

The MDL typically operates two shifts a day, five days a week. During periods with no fab operations, UPW continues to flow through all the wet benches in order to minimize the growth of bacteria. Since this UPW participates in no rinsing operations but just flows through the wet bench plenum, it is of higher quality than the water discharged during normal rinsing operations. The higher quality of the water entering the collection tank during these hours is particularly evident over most weekends when no fab activity is underway. To a lesser degree the discharge water collected during the graveyard hours of each workday (0100 to 0500) show a similar shift to higher quality. During the hours of normal fab operation, however, the water discharged from the wet benches is of significantly lower quality than UPW.

The quality of the spent rinse waters is probably much worse in the MDL than in many production fabs because the MDL wet benches do not include timers or other controls for separating the first rinse water from later rinses of a chemically processed lot of wafers. In addition, draining of the chemical baths themselves shares some of the same plumbing used to feed rinse water to the collection tank. The present procedure is to manually switch the plenum drain lines to the AWN tank prior to initiating the bath dump and to wait 2 hours following the bath dump before returning the plenum discharge water to the collection tank. Nonetheless, trace residues from the chemical bath dumps can still be swept into the collection tank when normal operations are resumed. Because of this arrangement, the MDL presents a more severe challenge for recycling than the typical production fab. On the other hand, the breaks in fab activity that characterize the MDL operations provide an opportunity to introduce recycling under lower risk conditions than are normally available in full scale production environments.

The first stage of introducing recycling of the "C*" streams to the MDL is monitoring of the properties of the collected "C*" rinse waters and deciding upon criteria of acceptance for return to a specific node of the UPW system. Figures 4 and 5 are plots of data collected from the start of Friday morning, September 25, 1998 at 0000 hrs until 2400 hrs on the following Thursday, October 1, 1998. These plots are typical of the properties that have been logged more or less continuously since the repaired collection tank (it had developed a leak) was reinstalled in the MDL recycle system in July 1998.

The varying activity states of the fab led to three classifications of rinse water quality: weekend water, overnight water and production-time water. The water properties plotted in Figure 4 and 5 illustrate the differences among these three states of fab activity. In Figure 4 the resistivity of the water collected in the tank, read from the left hand ordinate scale of the figure, exceeds 1 MΩ-cm from early Friday evening until early Monday morning. As wafer processing operations begin on Monday, 9/28, the tank resistivity falls to the low kΩ-cm range and remains low throughout the 2-shift workday with only brief excursions above 100 kΩ-cm. Between Monday night and Tuesday morning, the rinse water in the collection tank again reaches resistivity values in excess of 1 MΩ-cm. This pattern repeats during the rest of the week with the tank water resistivity significantly increasing after midnight on each day (although not always >1 MΩ-cm) and falling back to the single digit kΩ-cm range during most of each workday.

The other measures of water quality follow a similar pattern. For example, the pH of the tank water is slightly below 6 over the weekend but varies between the 9 - 10 range and the 2 - 3 range during the workday. Overnight, pH returns to the 4.5 - 7 range. ORP remains about 400 mV over the weekend and returns to that range overnight after being <100 mV or > 500 mV during much of the working day. Feedline pH and resistivity oscillate wildly during daily wet bench operations but settle down during the weekend and overnight. At present, however, the tank readings are the only readings that determine divert/recycle decisions based on pH and resistivity.

Figure 5 plots dissolved silica, NVR and TOC over the same time period. This plot also tabulates total water volume pumped to recycle or the AWN by the recycle pump. This value is displayed as a running total read from the left hand ordinate in m^3 and the total volume for the time period displayed appears in a labeled box at the bottom center of the figure. The rinse water flowrate into the collection tank from the fab, also read from the left-hand ordinate, is plotted inliters/min. It decreases when individual wet benches are diverted from the collection tank to

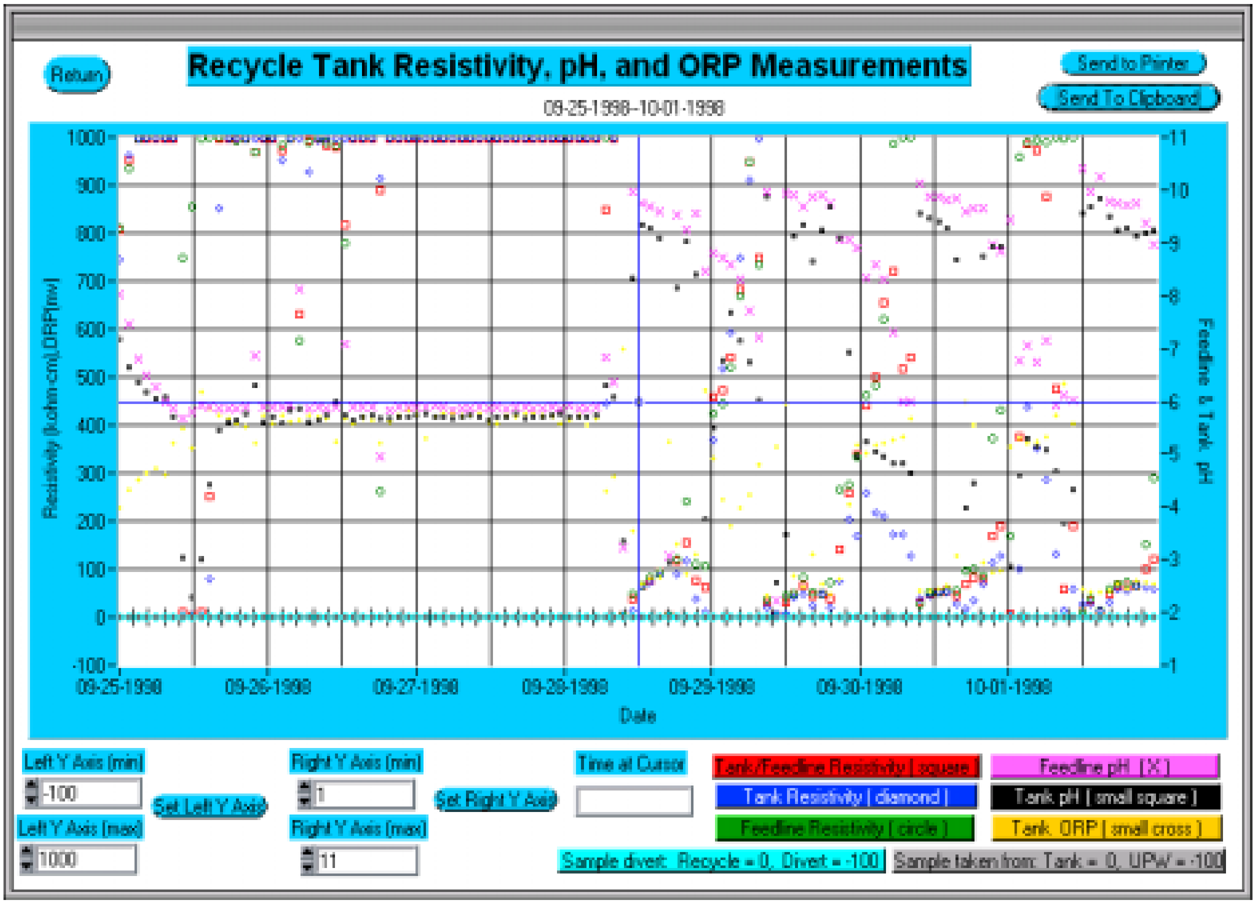

Figure 4. Chart 1 of Rinse Water Properties, 9/25/98-10/1/98

the AWN, as in the procedure for dumping chemical baths, or when performing wet bench maintenance. Over the weekend, dissolved silica, TOC and NVR are below 20 ppb, although the NVR doesn't reach that level until late Saturday night. Dissolved silica does not increase much during the week, either during the day or overnight. TOC exhibits some excursions to the 40 - 60 ppb range toward the end of the 2^{nd} shift each day. NVR generally increases to >500 ppb during work days and typically recovers overnight to values in the 100 - 300 ppb range.

The software used to read the data files and make plots includes provisions for changing the ordinate scales and for the time marking of specific events so that correlating readings between plots such as those illustrated in Figs 4 and 5 and fab activities becomes simple and accurate. The software also allows the data plots to cover any number of days between 1 and 7 and to plot as many as 2880 data points over the selected time range. Not plotted at present but logged in the data files are the water flowrates through the various loops of the sampling manifold and the recycle line. A total of 21 parameters are logged as 30 s averages, 15 of which can be plotted with the present software.

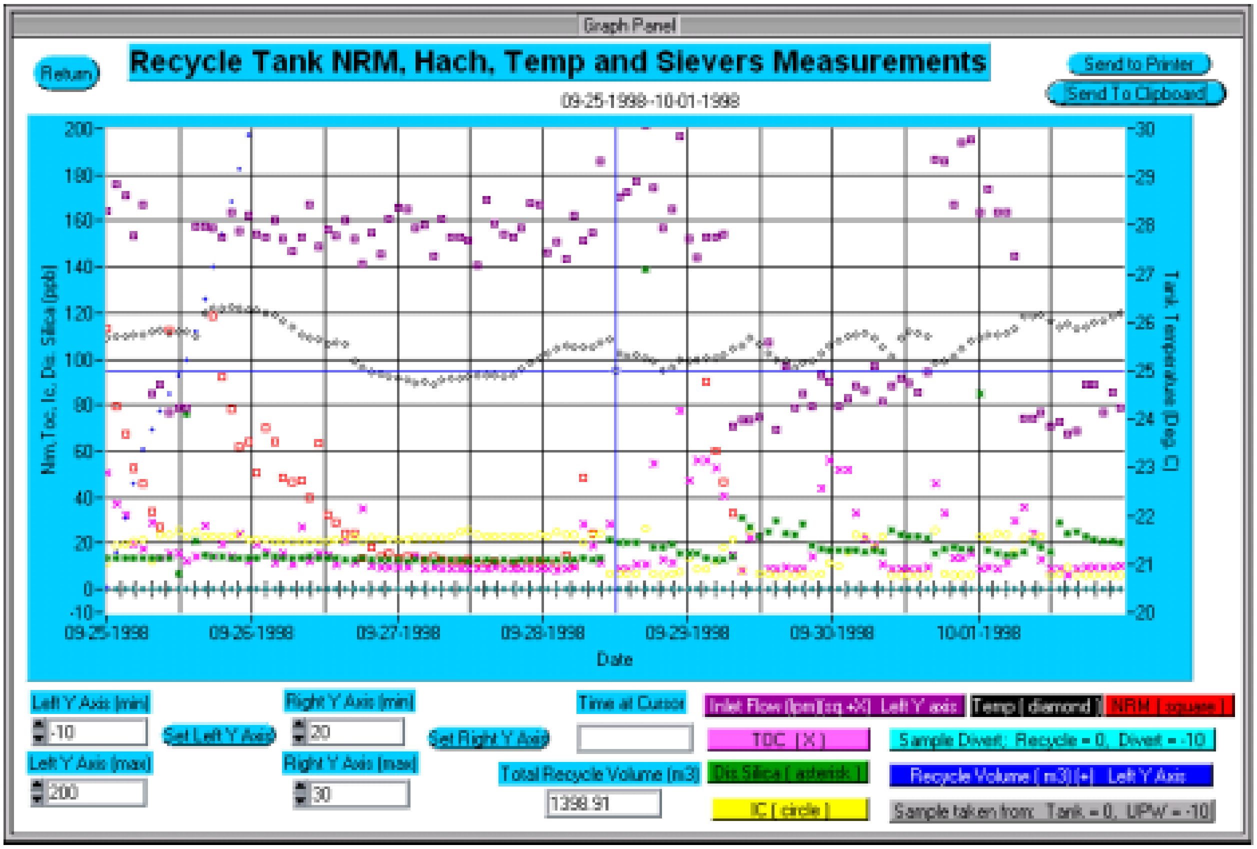

Figure 5. Chart 2 of Rinse Water Properties, 9/25/98 - 10/1/98

Tabulation of Rinse Water Properties

On-line measurements

Weekend rinse water

Resistivity: ~ 1 MΩ-cm or better (maximum value logged);

pH: 5-6

NVR: <20 ppb;

Dissolved silica: < 10 ppb

TOC: ~10 ppb

Nighttime (0100 - 0500) rinse water during the week

Resistivity: 300 - > 1000 kohm-cm;

pH: 4.5 - 7

NVR: as low as 40 ppb;

Dissolved silica: < 40 ppb

TOC: < 60 - 80 ppb

Daytime rinse water (1st & 2nd shifts- 0500 to 0100)

Resistivity: as low as 2 kohm-cm (logging did not extend below this value);

pH: 1- 11

NVR: > 500 ppb (maximum value read by the monitor);

Dissolved silica: <40 ppb

TOC: < 80 ppb

Off-line measurements on isolated grab samples

Weekend rinse water

Ionic concentrations and other properties:	Table 4
Trace metal concentrations:	Table 5

These properties compare favorably with similar properties of R/O product water from the MDL UPW system:

Ionic concentrations and other properties:	Table 6
Trace metal concentrations:	Table 7

Note that the ionic concentrations in Table 6 are reported in ppm and those in Table 4 are given in ppb. Because of the higher quality of the weekend rinse water, the analyses of these waters were conducted with analyzers having more sensitive detection limits. While the grab samples on which these measurements were made were collected several weeks apart, the conclusions of the comparison are assumed to be generally true.

These off-line data and the previously summarized on-line data support the goal of recycling the typical weekend water to the R/O product water tank without further treatment.

<u>Daytime rinse water, acidic extreme</u>

Ionic concentrations and other properties	Table 8
Trace metal concentrations	Table 9

By many metrics of contamination, even this "worse case" daytime rinse water compares favorably with R/O product water. However, it contains measurable concentrations of metals that are not present in the R/O product water and very high concentrations of chloride, phosphate and ammonium that need to be reduced before being compatible with recycling to the R/O tank. However, when compared to the properties of the incoming municipal water feeding the Sandia UPW plant (Tables 10 and 11), the daytime rinse water is clearly of superior quality. Virtually all contaminant concentrations are dramatically lower in the "worse case" daytime rinse water than in the municipal feed water (Table 10 ionic concentrations are in ppm while Table 8 ionic concentrations are in ppb). The pH of the daytime rinse water in this particular grab sample is low but the pH of daytime rinse water sometimes exceeds 10. TOC invariably is much lower in the water presently being collected in the recycle tank than in the municipal water.

Anomaly

Using a large tank to collect rinse waters from a number of different wet benches, while simpler to install than recycling hardware at the individual bench level or even among a grouping of similar benches, results in a large volume of water containing low concentrations of heterogeneous contaminants. Such water is invariably more difficult to purify than more homogeneously contaminated water [Ref. 2]. In addition, the mixing of a large variety of trace contaminants creates an environment in which unexpected and often undesirable chemical reactions can occur. A persistent, puzzling observation in the data already collected is reported in this section and is potentially evidence for such chemical activity.

This anomaly is most easily observed during the transition between periods of fab activity and inactivity. Rinse waters of low resistivity characterize fab activity, while the rinse water reaching the collection tank during periods of no fab activity has high resistivity. Typically, when fab activity ceases, as it does late Friday evening, the data logs show a rapid rise in the resistivity of the feed water to the collection tank (slipstream curve, Figure 6), followed by a

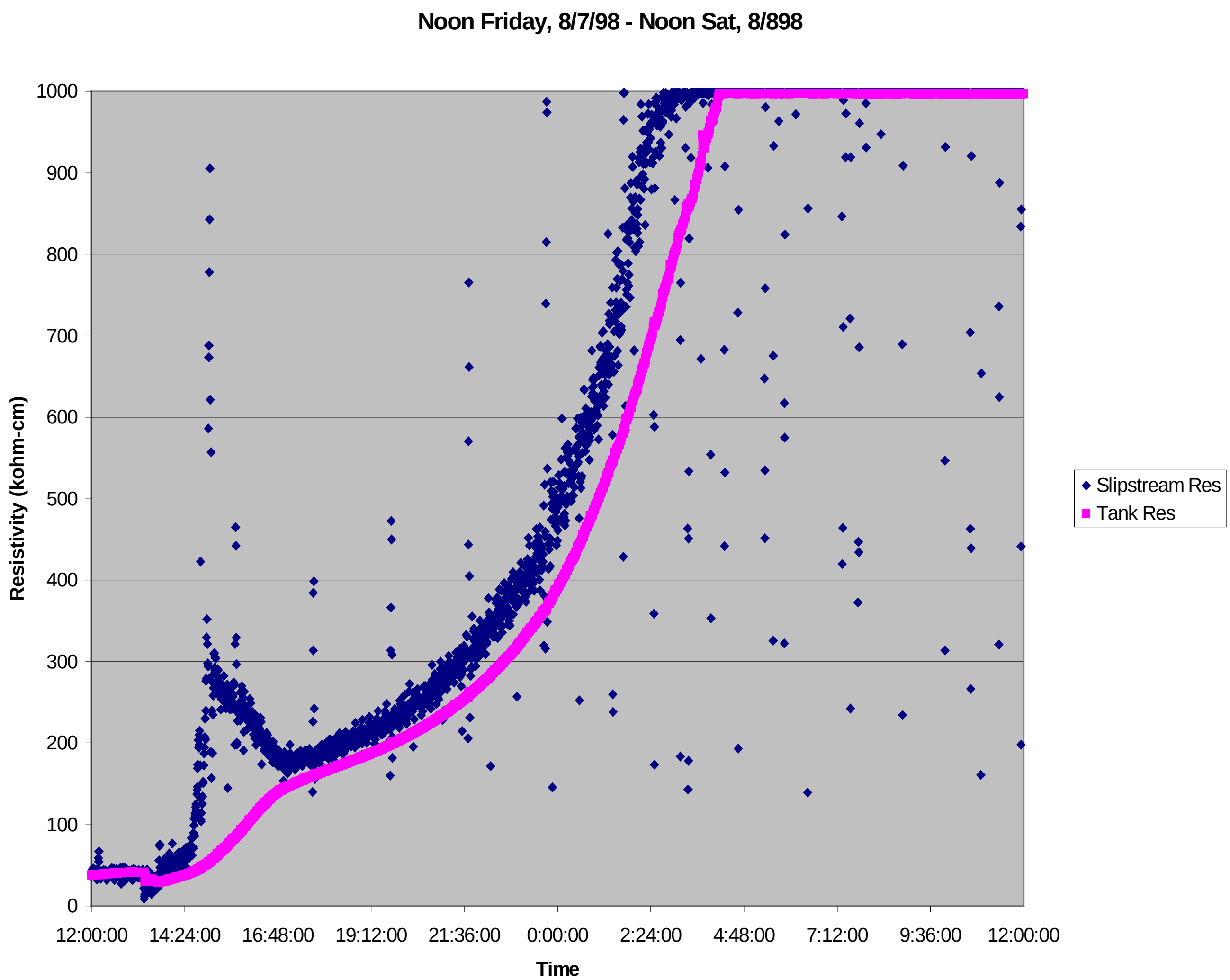

Figure 6. Tank Resistivity Trailing Slipstream Resistivity

corresponding but slower rise in the resistivity of the tank water. On some days, however, the observed behavior deviates from this pattern. At these times (Fig. 7), the feed water resistivity rises as normal and the tank resistivity follows up to a point, after which it begins to decrease, even though the feed water resistivity may have continued to rise to values that are off-scale high.

The periodic observation of this pattern correlates somewhat with a decrease in tank pH and the presence of TOC in the tank water (Figs. 8 and 9, respectively), suggesting that chemical oxidation of the TOC creates a conductive species in the tank that is not part of the feed water stream from the fab.

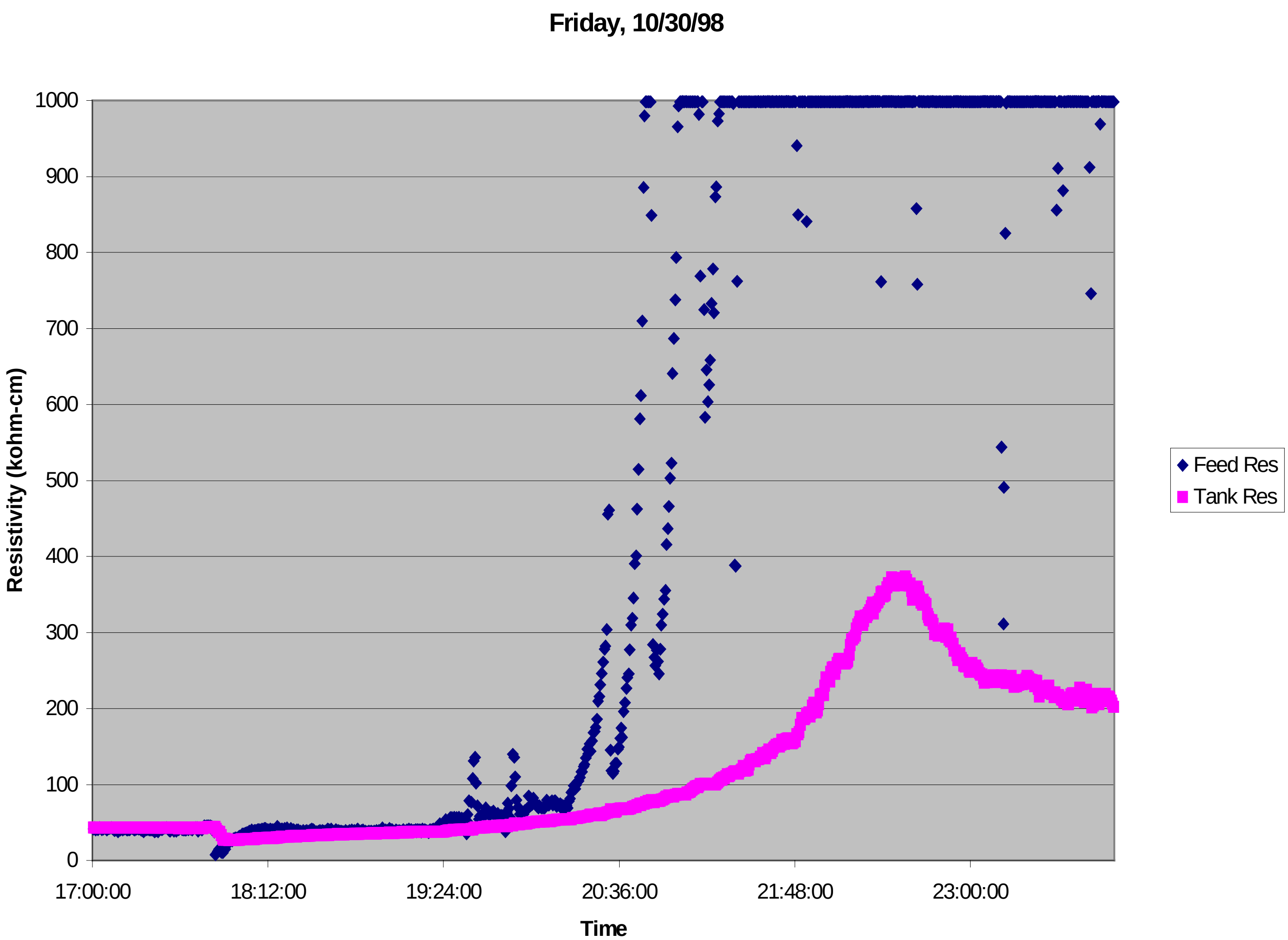

Figure 7. Anomalous Behavior of Tank Resistivity

The rise in IC accompanying the fall in pH (Fig. 9) is typical but is most likely a measuring artifact. At high pH, inorganic carbon is mostly carbonate or bicarbonate with negligible concentrations of carbon dioxide. If the acid injected into the water sample by the TOC analyzer does not lower its pH to a value of, say, 4 or less, much of the inorganic carbon will not be detected by the resistivity cell of the TOC analyzer that measures total inorganic carbon. With water samples of neutral or low pH, the acid added to the water sample by the analyzer easily reduces its pH to the range in which the inorganic carbon is effectively 100% carbon dioxide, making it readily measurable by the analyzer. What causes the pH to change during these off-hours of the fab is not known but is postulated to be additional evidence for tank chemistry.

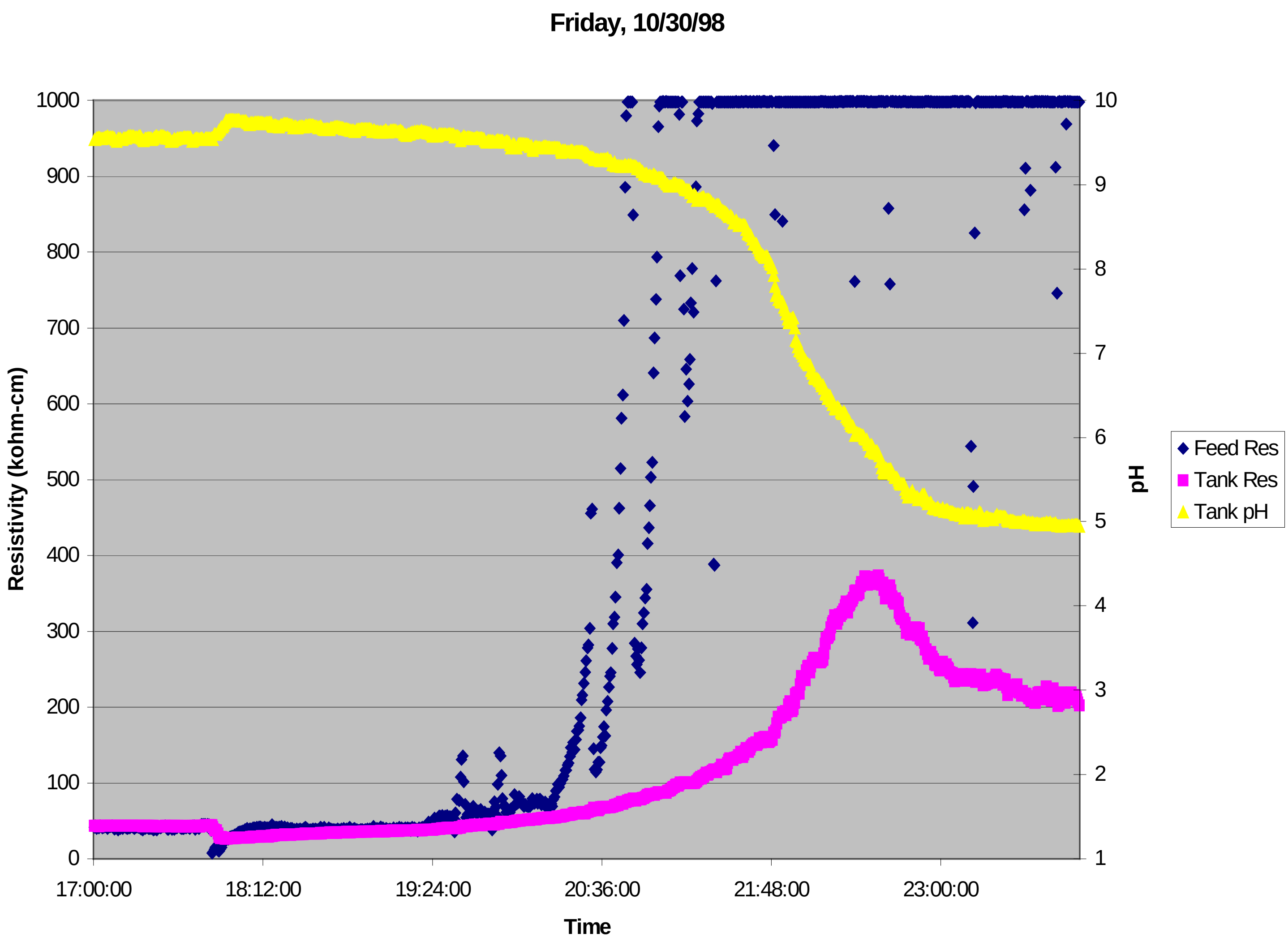

Figure 8. Correlation of Anomalous Behavior with Tank pH

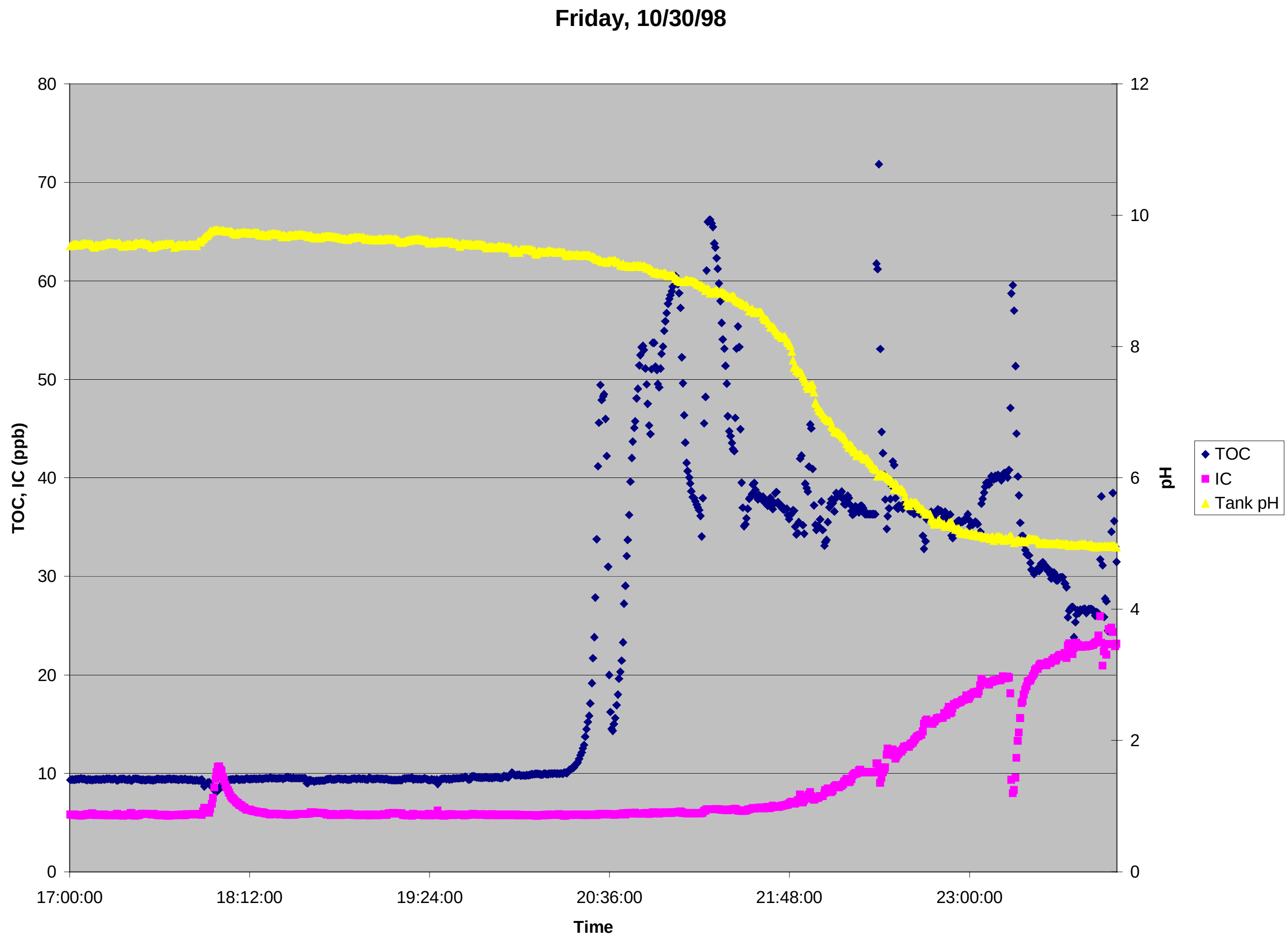

Figure 9. TOC Increase Prior to Anomalous Tank Resistivity Behavior

Summary: Status and Plans

The flowrate of rinse waters to the recycle collection tank averages about 40 gpm when all the "C*" wet benches are connected to the collection tank. This flowrate is about 40% of that discharged at present to the municipal sewer system by the AWN. None of the rinse water collected by the recycle system has yet been recycled to the plant UPW system. The recycle loop remains in the monitoring and checkout phase. The present recycle configuration needs to be modified to provide the needed delay times for adequate protection against rapid (concentration buildups on the order of seconds) increases in the concentration of TOC and other contaminants. Once such hardware is in place, a request to begin actual recycle operations by recycling just the weekend water will be resubmitted to fab management. This first, minimum risk step alone, recycling just the idling UPW weekend water flows from the wet benches without further treatment, represents about a 12% reduction in the water volume discharged from the AWN. As the addition of treatment modules in the recycle loop leads to the acceptability of recycling overnight water and some of the daytime water, the percentage of recycled water will grow. The addition of various "Q" streams (Table 3) to the recycle loop will also lead to increased percentage of recycled water from the fab. The goal of the project is to recycle 50% or more of the present AWN discharge. The impact of recycling at this level upon the reclaim operation under which water discharged from the AWN now feeds the building cooling towers is not clear.

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Biographies

Robert P. Donovan is a process engineer assigned to Sandia National Laboratories as a contract employee by L & M Technologies, Inc. In addition to the demonstration of rinse water recycling described in this paper, his project work at Sandia has included the assessment of analyzers for the rapid, continuously on-line measurement of TOC in rinse waters and the evaluation of prototype water purification equipment for upgrading the quality of rinse waters.

Dennis J. Morrison is a biologist in the Environmental Monitoring and Characterization Department of Sandia National Laboratories. He conducts environmental monitoring studies in support of projects in aerosol science, atmospheric monitoring and water conservation. He set up the instrumentation used in the water recycling development and wrote the software for data logging and control of the recycle system. He operates and maintains all analyzers and instruments used in the recycle system.

Robert P. Timon is a Member of the Technical Staff in Sandia's Microelectronics Development Laboratory. He is responsible for wet bench operations and maintenance throughout the fab and the performance of the wet cleans conducted within these stations.

John DeGenova is a senior member of the technical staff of Texas Instruments. He is presently working on his PhD degree in Chemical Engineering at the University of Arizona-Tucson. He received an MS degree in Environmental Engineering in 1987 from the University of Texas at Austin, and received a BS degree in Chemical Engineering in 1983 from the University of Missouri at Rolla. Since joining TI in 1983, he has been a first line supervisor and process engineer in circuit board manufacturing and a facilities engineer in the wafer fab design and construction projects. His responsibilities have included the Ultrapure Water and Wastewater treatment facilities. He has been involved with the recycling and reclamation of water since 1987, and has been responsible for the installation of UPW recycle systems at TI wafer fabs. He is a registered professional engineer in the state of Texas. From 1996 through 1998, he was a TI assignee to SEMATECH where he served as leader of the Project Technical Advisory Board for S116, Water Conservation.

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